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# EFFECT OF ACID CATALYST TYPES AND CONCENTRATION ON ESTERIFICATION PRE-TREATMENT OF NON-EDIBLE OIL FOR BIODIESEL PRODUCTION

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**ABSTRACT**

In this study, crude *Calophyllum inophyllum* oil was used as the feedstock for biodiesel production. This feedstock contain high acid value of 56.3 mg KOH/g (28wt%) which is not favorable for direct conversion to biodiesel by transesterification. Therefore, this paper emphasizes the study on the pre-treatment process of degumming and acid catalyst esterification in order to reduce the high free fatty acid for successful transesterification. Single parameter study was conducted to identify the best acid with best concentration to efficiently esterify the degummed *Calophyllum inophyllum* oil with highest FFA conversion. Among phosphoric acid, hydrochloric acid, and sulphuric acid, 3.0M concentration of sulphuric acid was found to be the best condition for the esterification reaction providing 87.46% FFA conversion.

**Keywords:** biodiesel, *Calophyllum inophyllum,* esterification, degumming

**NONMENCLATURE**

| *Abbreviations* | |
|---|---|
| CI | *Calophyllum inophyllum* |
| FAME | Fatty Acid Methyl Ester |
| FFA | Free fatty acid |

## 1. INTRODUCTION

The properties of biodiesel or chemically known as fatty acid methyl ester (FAME) have been proven to be similar with petroleum-based fuel in extensive number of studies [1–8]. This has prompted the research for biodiesel development in order to replace the fossil fuel consumption as a step in reducing the GHG emission and dependency on fossil fuel. In 2013, biodiesel is considered as the second largest category of biofuels, accounting for 26.12 billion liters worldwide [9]. The advantages of biodiesel compared to petroleum derived fuel include the production from renewable resources, biodegradable, lower toxicity, superior lubricity, higher flash point and cetane number, can be blend in any proportion of diesel and adaptability in diesel engine without any major modification [3].

Biodiesel can be derived from vegetable oil or animal fats, reacted with an alcohol (usually methanol) through a process called transesterification reaction. However, the conversion of biodiesel from edible vegetable oil has created the issues with the rivalry of food for human and fuel basis consumption, deforestation for spacious area of agriculture, and the rise in vegetable oil prices. Non-edible biodiesel feedstock are gaining global attention due to the worldwide availability of the resource, environmental friendly, more economical compared to edible oil, and able to abridge the competition for food. Non-edible oils such as *Jatropha curcas,* Karanja, *Ceiba petandra*, *Calophyllum inophyllum* and etc are found to be the plausible options as biodiesel feedstock compared to edible oil. Among the mentioned non-edible feedstocks, *Calophyllum inophyllum* (CI) was found to provides various advantages such as up to 50 years of survival

potency, possesses higher oil yield than *Jatropha*, high flash point and heating value [4,9].

Despite the advantages of the CI feedstock, high FFA content of the crude oil are not favorable by transesterification reaction. This will create undesirable soap formation in which will reduce biodiesel yield. Therefore, this necessitates a pre-treatment step to reduce the FFA level in the oil to the acceptable range of FFA in the oil for biodiesel production which is around 2% or less [10]. The pre-treatment step involves acid esterification of FFA in the presence of solvent (methanol) and an acid catalyst producing fatty acid ester and water. Esterification reaction is a simple process but it plays a very crucial role in optimizing the yield of the end product. The process will reduce the excess FFA concentration in the oil and alleviate the chances of soap formation in the alkaline transesterification step.

Considering the crucial part for producing biodiesel from extremely high FFA content of CI oil, the present study will highlight the pre-treatment step of acid catalyzed esterification from high FFA CI oil in order to reduce the FFA content to a considerable level (1-2wt %.) prior to transesterification reaction. The best type of acid catalyst and catalyst concentration were identified by single parameter study to determine the best acid catalyst and catalyst concentration to efficiently reduce the FFA content.

## 2. PRELIMINARY ESTERIFICATION REACTION OF CI OIL

### *2.1 Feedstock- Calopyllum inophyllum*

*Calophyllum inophyllum* is a multipurpose tree available from multiple origins including East Africa, South East Asia, India, Australia and the South Pacific. Currently, it has been planted throughout the tropics [3]. It grows best in sandy, well drained soils with around 100-200 fruits/kg of the tree yield [4]. The crude oil can be extracted from the kernels with very high oil content of 75%. C. Inophyllum oil is composed of free fatty acids, glycerides, sterols, terpenoids, steroids, calophyllolids, inophyllolids and calophyllic acid [11]. The crude oil is dark green and non-edible in nature with an aromatic odor and insipid taste, which is traditionally used as medicine, soap, lamp oil, hair grease and cosmetics in different parts of the world.

Fatty acid composition is an important property for any biodiesel feedstock. The compositions will highly influence its properties. Table 1 shows the composition of fatty acid in the crude CI oil based on literature [12]. Fatty acid compositions of CI oil were found to mainly dominated by oleic acid (C18:1) followed by linolenic acid (C18:2), stearic acid (C18:0) and palmitic acid (C16:0).

Table 1 Fatty acid compositions of CI oil [12]

| Fatty acid | Formula | Structure | wt.% |
|---|---|---|---|
| Myristic acid | $C_{14}H_{28}O_2$ | $C_{14:0}$ | 0.09 |
| Palmitic acid | $C_{16}H_{32}O_2$ | $C_{16:0}$ | 14.6 |
| Palmitoleic | $C_{16}H_{30}O_2$ | $C_{16:1}$ | n/a |
| Stearic acid | $C_{18}H_{36}O_2$ | $C_{18:0}$ | 19.96 |
| Oleic acid | $C_{18}H_{34}O_2$ | $C_{18:1}$ | 37.57 |
| Linoleic acid | $C_{18}H_{32}O_2$ | $C_{18:2}$ | 26.33 |
| Linolenic acid | $C_{18}H_{30}O_2$ | $C_{18:3}$ | 0.27 |
| Arachidic acid | $C_{20}H_{40}O_2$ | $C_{20:0}$ | n/a |

### *2.2 Esterification reaction for biodiesel production*

In this study the FFA level of CI feedstock exceed the permissible limit and was not possible for direct transesterification reaction to produce biodiesel. Therefore, pre-treatment step was necessary. Among the available pretreatment methods such as steam distillation or extraction of alcohol and acid-catalyzed esterification, esterification of FFA with methanol in the presence of acidic catalyst is the most commonly used method because of its simplicity and utilization of acid catalyst to convert FFAs into biodiesel [3].

Esterification reaction involves the reaction of fatty acid with alcohol i.e methanol in the presence of an acid catalyst. The reaction is as depicted in Equation 1 below:

$$\underset{(Fatty\ acid)}{RCOOH} + \underset{(Methanol)}{CH_3OH} \xrightarrow{H_2SO_4} \underset{(Fatty\ acid\ ester)}{RCOOCH_3} + \underset{(Water)}{H_2O} \quad \text{Eq.1}$$
$$(Sulph.\ acid)$$

Where R is a fatty acid alkyl group.

Esterification reaction can be clearly explain by the following steps [13]:

(1) Initial protonation of the carboxylic acid to give an oxonium ion
(2) The oxonium ion and an alcohol undergo an exchange reaction to give the intermediate
(3) Lose a proton to become an ester

### *2.3 Materials*

Dark green crude CI oil was procured from Indonesia. Methanol was deployed as the reactant for esterification reaction. Phosphoric acid (85%) was used for pre-treatment process during degumming. Sulphuric acid, phosphoric acid and hydrochloric acid were used

as the catalyst for esterification reaction. Potassium hydroxide was used as the titrant for acid value determination.

### *2.4 Methods*

Pre-treatment process of CI oil which possesses extremely high FFA content was conducted through two stages – degumming and acid-catalyzed esterification reaction. At initial stage of degumming, gums and other mucilage were removed from the crude oil. Then, acid-catalyzed was carried out to significantly remove the FFA in the oil by converting it into esters. The reduction of FFA must be below 2 wt% prior to transesterification. The lab-scale setup for esterification reaction is shown in Figure 1.

#### *2.4.1 Degumming of crude CI oil*

Crude CI oil contains gums such as phosphate, protein, carbohydrate, water residue and resin. Therefore, in the initial stage, there is a need to separate and remove all the mucilage and phospholipids from the oil through degumming process in order to improve the oxidization stability of the oil, significantly reduce acid value, and prevent the impurities to interfere the biodiesel production later on. 500 ml of crude CI oil was preheated at 60 ℃ with stirring speed of 450 rpm. 3 vol.% of 85% phosphoric acid, $H_3PO_4$ was added dropwise to the preheated crude oil and the solution was stirred for 30 minutes at constant 60 ℃. Once the reaction was complete, the mixture was centrifuged at 2000 rpm to separate the phosphate compounds from the oil. Next, the degummed oil was washed with 60 ℃ warm water to remove any impurities left. Then, the oil was heated at 100℃ to remove excess water.

#### *2.4.2 Esterification reaction*

The conversion from high free fatty acid feedstock requires a pre-treatment process with acid catalyst to reduce the acid value to 2 wt.% prior to the transesterification reaction [4,14]. Single parameter study for few types of possible acids potentially in reducing the FFA content in the degummed oil such as sulphuric acid ($H_2SO_4$), hydrochloric acid (HCl) and phosphoric acid ($H_3PO_4$) was first conducted. The parameter conditions were fixed for all type of acids with catalyst loading 15 vol.% of 1.0 M acid concentration and methanol (20:1 methanol to oil molar ratio) were added to the pre-heated degummed oil at 65 ℃. The mixture was stirred at 500 rpm with constant 65 ℃ reaction temperature for 2 hours. On the completion of the reaction, the mixture was further heated uncovered until the methanol was completely evaporated. Next, acid catalyst that provides the best FFA conversion was pursued to determine the best catalyst concentration used in reducing FFA content. The reaction was conducted to study the best catalyst concentration of 1.0, 2.0 and 3.0 M while keeping the other parameters of catalyst loading, methanol to oil molar ratio, reaction temperature and reaction time fixed and remains unchanged.

Figure 1 Esterification reaction setup

#### *2.4.3 Analysis of Free Fatty Acid*

The determination of acid value of oil sample was conducted through KOH titration. Few drops of phenolphthalein was added to 5 g of oil samples as an indicator until both solution was well-mixed. Then, the mixture was titrated with 0.1 M KOH until light pink colour appeared permanently. The calculation of acid value was calculated based on Equation 2:

$$AV = \frac{V_{KOH} \times N_{KOH} \times MW_{KOH}}{W_{oil}} \quad \text{Eq. 2}$$

Where AV is acid value, $V_{KOH}$ is the volume of KOH consumed, $N_{KOH}$ is the molarity of KOH which is 0.1 M,

$MW_{KOH}$ is the molecular weight of KOH which is 56.1 g/mol and $W_{oil}$ is the weight of oil sample.

### *2.5 Results and discussions*

#### *2.5.1 Characterization of crude CI oil*

The crude CI oil has a dark green colour with a disagreeable taste or odour. The properties of crude CI oil are tabulated in Table 2 below. Based on its saponification value, the average molecular weight of the oil was calculated from Equation 3 below.

$$MW = \frac{3\times1000\times56.1}{SV} \quad \text{Eq.3}$$

Where MW is Molecular weight, and SV is the saponification value.

#### *2.5.2 Degumming of CI oil*

After degumming of oil, the dark green colour of crude oil turned reddish yellow as shown in Figure 2. Two separation layers formed where darker and viscous layer of phospholipids resided at the bottom while degummed oil resided at the upper layer. The separation is shown in Figure 3. Degummed oil provides better property compared to crude CI oil in terms of viscosity and acid value.

Figure 2 Left: Crude CI oil, Right: Degummed CI oil

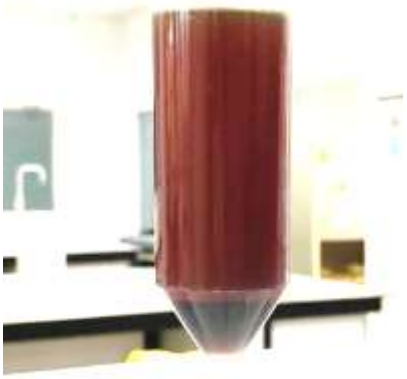


Figure 3 Separation layer of gums and CI oil

Table 2 Properties of crude and degummed CI oil

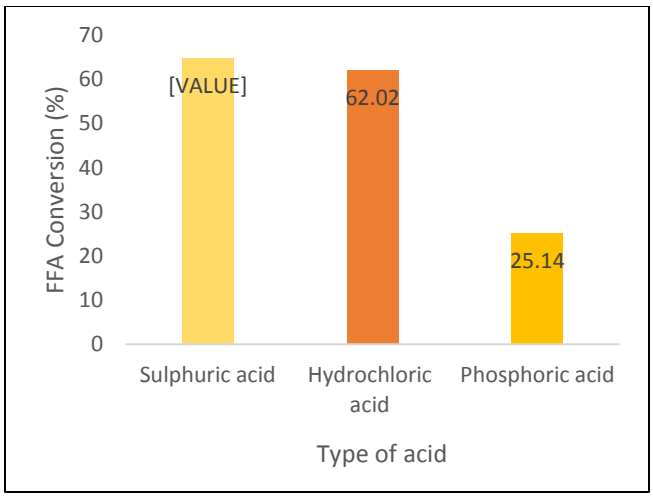
| **Properties** | **Crude CI oil** | **Degummed CI oil** |
|---|---|---|
| Acid value (mg KOH/g) | 56.3 | 49.9 |
| Saponification value (mg KOH/g) | 202.0 | n/a |
| Density (g/ml) | 0.9 | 0.86 |
| Molecular weight (g/mol) | 833.17 | n/a |
| Colour | Dark green | Reddish yellow |

#### *2.5.3 Esterification of CI oil*

##### *2.5.3.1 Type of acid catalyst*

Degummed oil was further continued for acid-catalyzed esterification for reduction in FFA content. This is the crucial part of the biodiesel production since transesterification will not success if the FFA content is still in the unfavourable level. The first single parameter study for type of acid catalyst was conducted to identify the best acid that efficiently convert the FFA content.

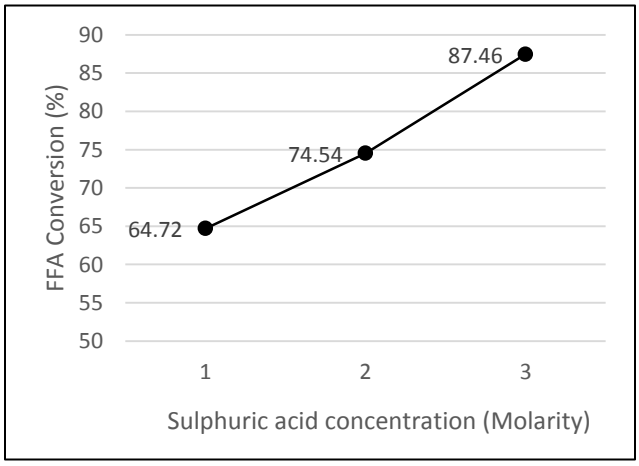
Based on the result from Graph 1, it can be said that sulphuric acid was the most efficient to convert FFA content in the degummed oil as much as 64.72% compared to hydrochloric acid (62.02%) and phosphoric acid (25.14%). This agrees with the fact that the best commercial acid catalyst for promoting esterification reaction was sulphuric acid where heavy neutralization process of the acid is unnecessary [15]. This explains why most studies use sulphuric acid for acid-catalyzed pre-treatment.




Graph 1 Effect of type of acid on the FFA conversion

*2.5.3.2 Concentration of acid*

Next, the best acid catalyst of sulphuric acid $H_2SO_4$ was used for further determination of best concentration of acid employed to sufficiently convert the FFA content. The concentration of sulphuric acid were varied by 1.0, 2.0 and 3.0 M. Graph 2 shows the result for FFA conversion depending on the concentration of sulphuric used to catalyze the reaction. The reaction of degummed oil with 3.0 M of sulphuric acid gives the best FFA conversion as high as 87.46%. As the concentration increases, the FFA conversion increases. Higher concentration of acid may speed up the reaction and forcing the equilibrium state of the reaction with higher conversion.




Graph 2 Effect of sulphuric acid concentration on the FFA conversion

## *2.6 Conclusions*

Production of biodiesel from non-edible *Calophyllum inophyllum* (CI) oil requires additional pre-treatment step in order to reduce the FFA content to 2wt% permissible for transesterification reaction. Acid-catalyzed esterification is the crucial part to reduce the high FFA content in the feedstock prior to transesterification reaction. In this study, the CI oil was first treated with 85% concentrated phosphoric acid to remove any gums and mucilages from the crude oil. Then, acid-catalyzed esterification was conducted by varying the type of acid catalyst of 1.0M concentration each used to catalyze the reaction. Sulphuric acid was found to be the promising catalyst with the highest FFA conversion of 64.72% followed by hydrochloric and phosphoric acid. As the concentration of sulphuric acid was increased to 2.0M and 3.0M, the higher the FFA conversion. Thus, the highest 87.46% FFA conversion was resulted from 3.0M of sulphuric acid was said to be the best condition in reducing the FFA content considering other parameters fixed. Further intense optimization study of other important parameters such methanol to oil molar ratio, reaction time, catalyst loading and reaction time are estimated to result in higher FFA conversion up to 90%.

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